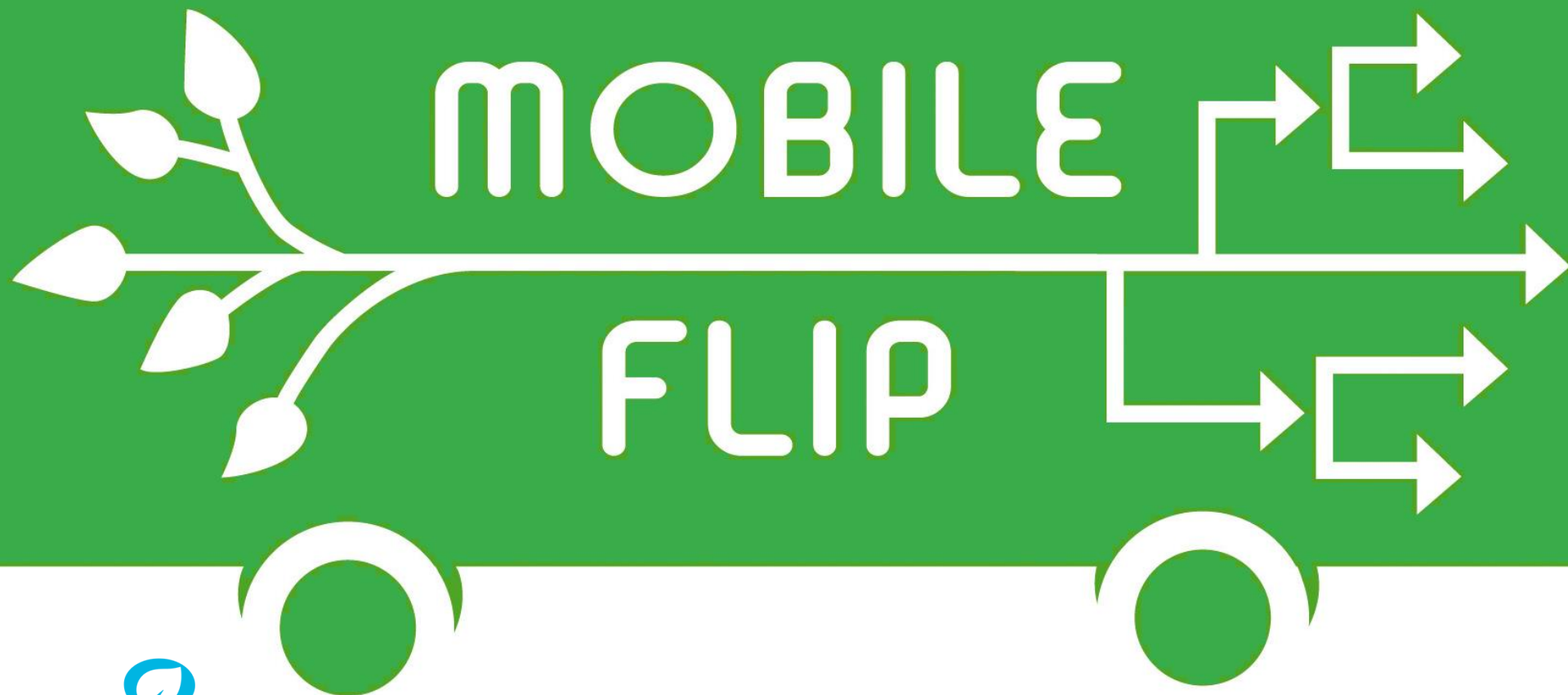




Biochar – Quality and Applications

Sippola 16.5.2018

Kimmo Rasa

Working group: Jari Hyväluoma, Riikka Keskinen, Jaakko Heikkinen, Minna Sarvi, Marleena Hagner, Helena Soinne

Natural Resources Institute Finland, Luke

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Content

- ✦ Processes and raw materials
- ✦ Chemical properties of biochars
- ✦ Physical properties of biochars
 - ✦ Micron-scale pore structure
- ✦ Applications
- ✦ Conclusions

Raw materials (red box)



Corn leaves

Wheat straw

Grape pomace

Scots pine bark

Green house residues



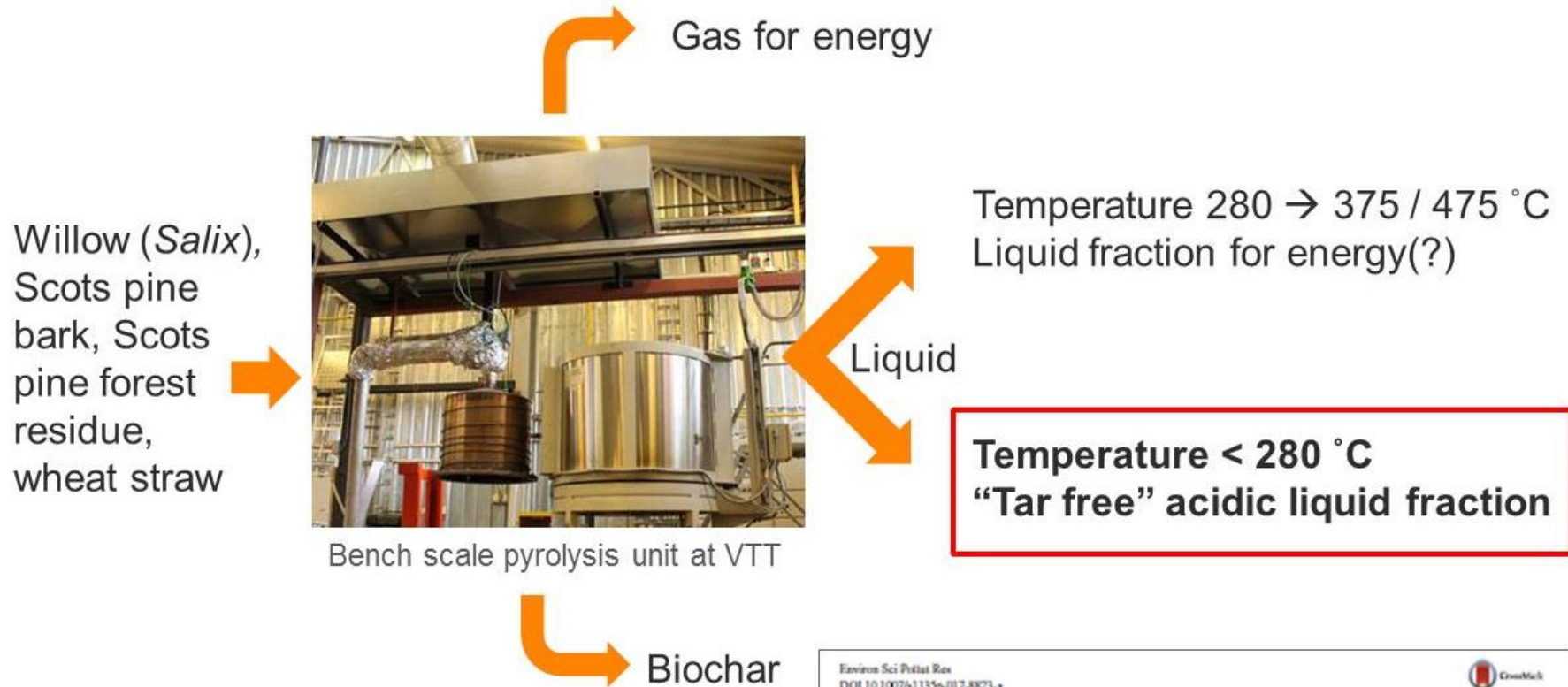
Corn stover

Brewery residues

Unbarked willow

Coffee cake

Laboratory scale pyrolysis vs. mobile demo-device



Environ Sci Pollut Res
DOI 10.1007/s11356-017-8823-x

ENVIRONMENTAL FUNCTIONS OF BIOCHAR

Quantitative characterization of pore structure of several biochars with 3D imaging

Jari Hyvärinen¹ · Sampo Kulju¹ · Markus Hannula² · Hanne Wäkeberg² · Anssi Kalli² · Kimmo Räsä¹

Hydrothermal Carbonization, HTC



10-l Hastelloy C276 stirred autoclave reactor at VTT

- 260 °C + pressure
- Batch type
- Suitable for initially wet biomasses
- Hydrochar ~ biochar

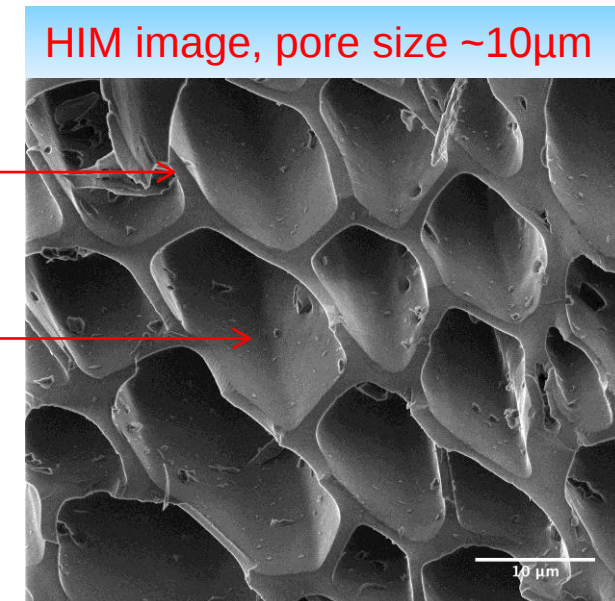
Chemical variation of biochars

- ✦ There is no "common biochar" but **biochars** with varying chemical properties
- ✦ Raw material **X** Process type **X** Process conditions = Biochar quality

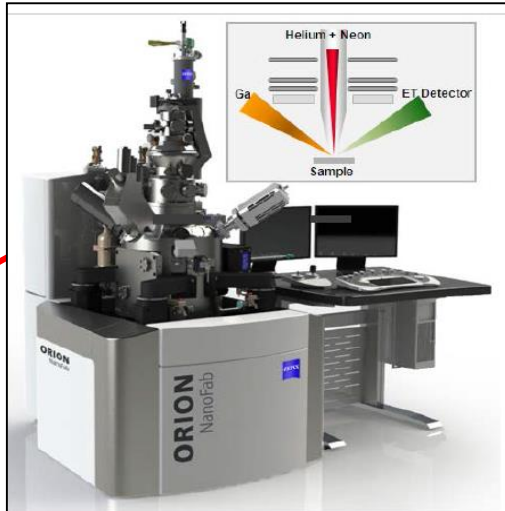
		Ash %	EC μS/cm	pH	Peak area cm-1	C %	O %	H %	N %	CEC	Ca mmol/kg	K mmol/kg	Mg	Na	PAH16
	TOR-SPR	0.6	114	5.4	0.43	53	41	5.8	0.1	81	43	14	9.1	nd	0.2
	SP-SPFR	4.8	318	9.0	0.05	88	8	3.2	0.9	16	191	87	12.6	0.5	10.0
Scots pine bark 375 °C	SP-SPB-L	3.1	165	8.0	0.09	79	17	3.9	0.4	136	89	51	9.9	1.4	24.5
Scots pine bark 475 °C	SP-SPB-H	3.5	190	8.4	0.06	87	10	3.1	0.5	20	239	50	3.6	0.6	3.8
	SP-WILL	4.5	462	9.3	0.08	87	8	3.2	0.9	34	459	120	23.2	2.8	4.4
Wheat straw	SP-WS	19.7	1520	10.0	0.08	87	9	3.1	0.7	88	169	424	66.3	2.3	5.2
Scots pine bark	HTC-SPB	1.9	105	4.1	0.38	73	22	5.1	0.4	278	18	0.3	nd	0.5	3.7
Willow	HTC-WILL	0.7	59	5.1	0.50	73	21	5.3	0.7	138	37	0.4	2.2	0.4	4.0
	HTC-CC	0.1	56	4.0	3.13	74	16	7.8	2.6	91	2	0.2	nd	0.1	2.7
	HTC-BRE	3.0	83	5.6	0.62	74	15	7.1	3.7	8	20	0.1	12.3	0.1	1.8

Physical properties - Pore structure of biochar

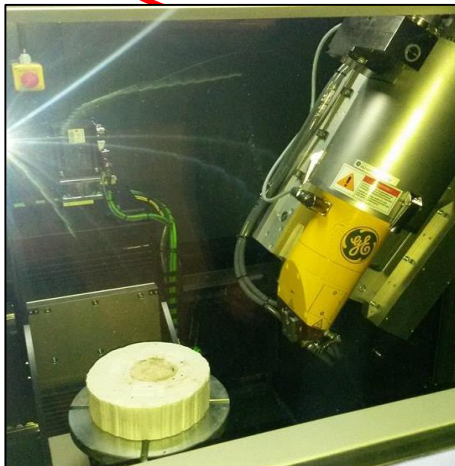
- ✦ Porosity is a fundamental property of biochar
 - ✦ Many applications rely on the pore system, especially on pore size distribution and pore continuity of biochars
- ✦ Biochar internal porosity is not well understood
 - ✦ Limitations of research methods
 - ✦ Gas absorption techniques → nano-scale pores
- ✦ Pores relevant for soil biological functions
 - ✦ Micron scale, $> 1 \mu\text{m}$
 - ✦ Water retention and transport properties
 - ✦ Bacteria, fungi, plant roots



X-Ray Tomography and Helium Ion Microscopy



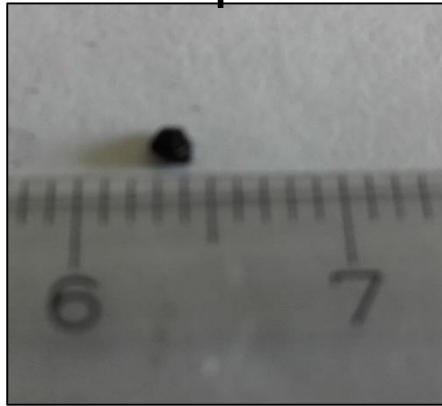
Subcontracting
and
cooperation
network



Flexible and resource
efficient use of cutting-
edge research methods

X-ray tomography & image analysis

Sample



Imaging



Raw data

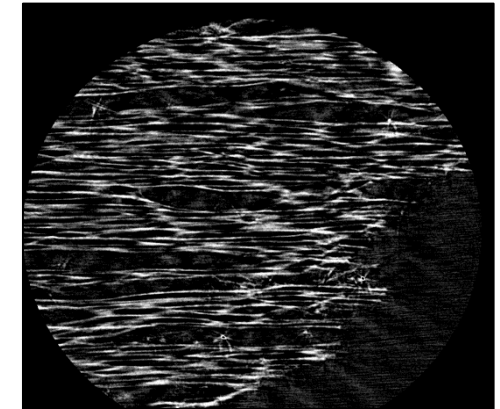


Image processing and visualization

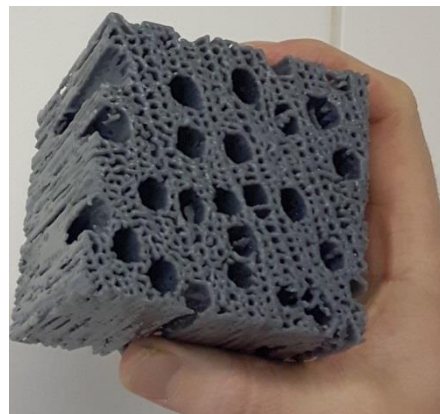
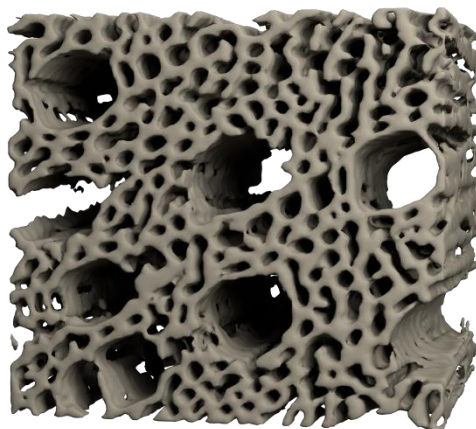
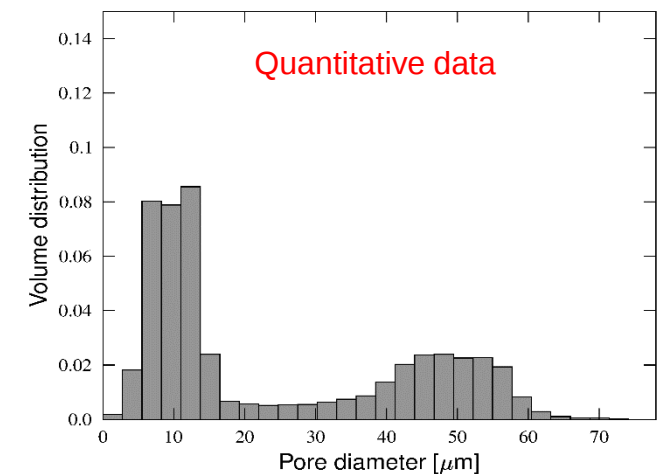


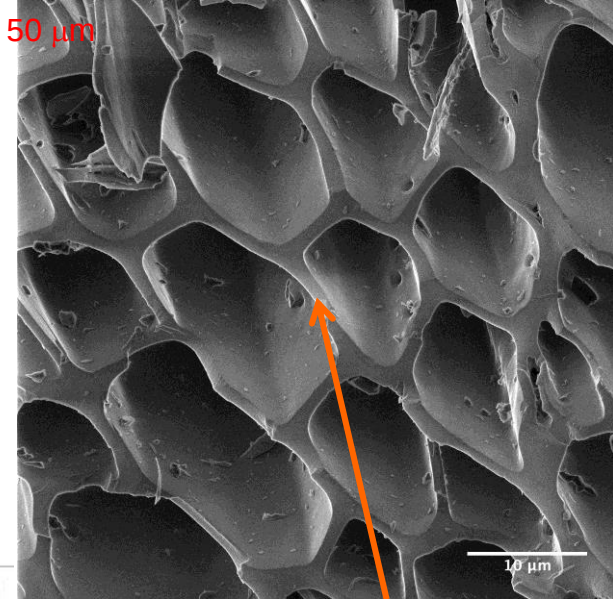
Image analysis



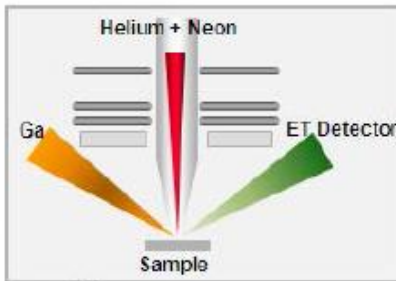
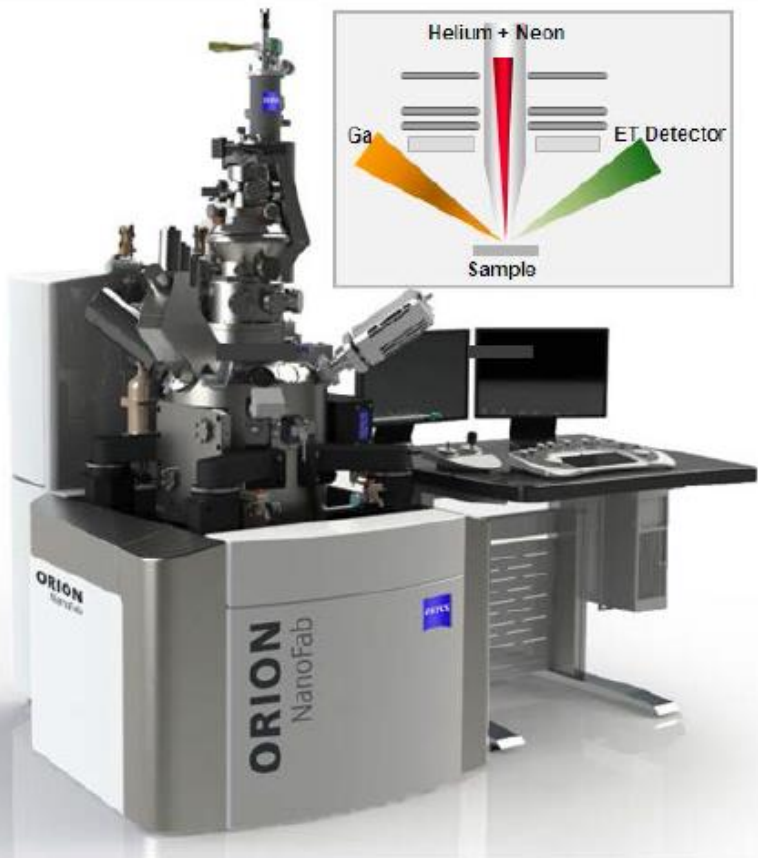
What about porosity smaller than imaging resolution?

Helium Ion Microscopy (HIM)

50 μm $\times$ 50 μm

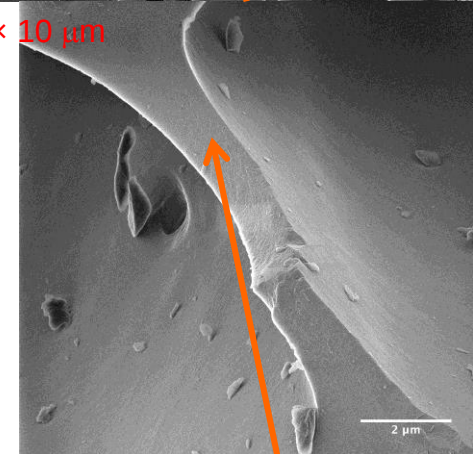


The ORION NanoFab Platform

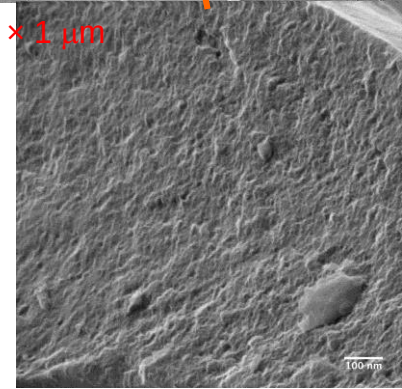


- 3D Nanofabrication of sub-10nm structures.
- **High Resolution Imaging (<0.5nm) ideal for nanoscale research.**
- **Precise Machining** with He/Ne beams and **Rapid Prototyping** with Ga beam – only platform offering unique combination of ion beams.
- **Configurable** architecture to address specific imaging and nanofabrication applications.

10 μm $\times$ 10 μm

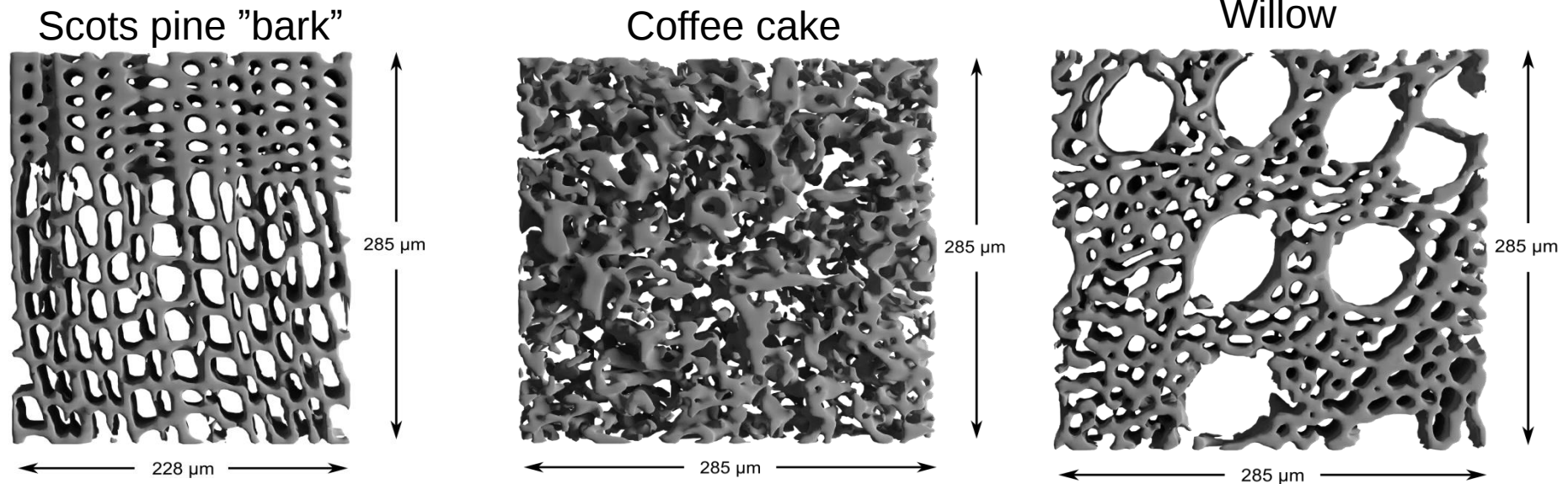


1 μm $\times$ 1 μm



Structural variability of biochars

- Difference in pore structure = difference in biochar functions
- **Biochar producer** → choice of raw material

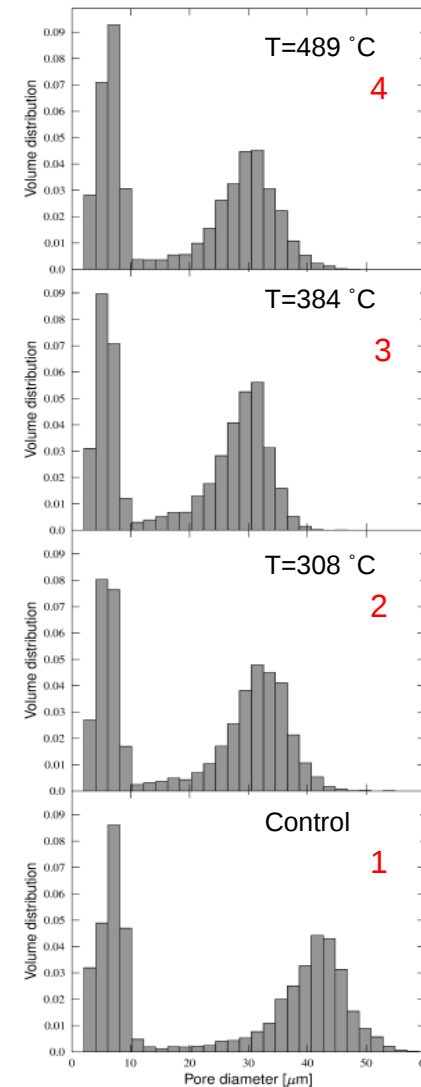
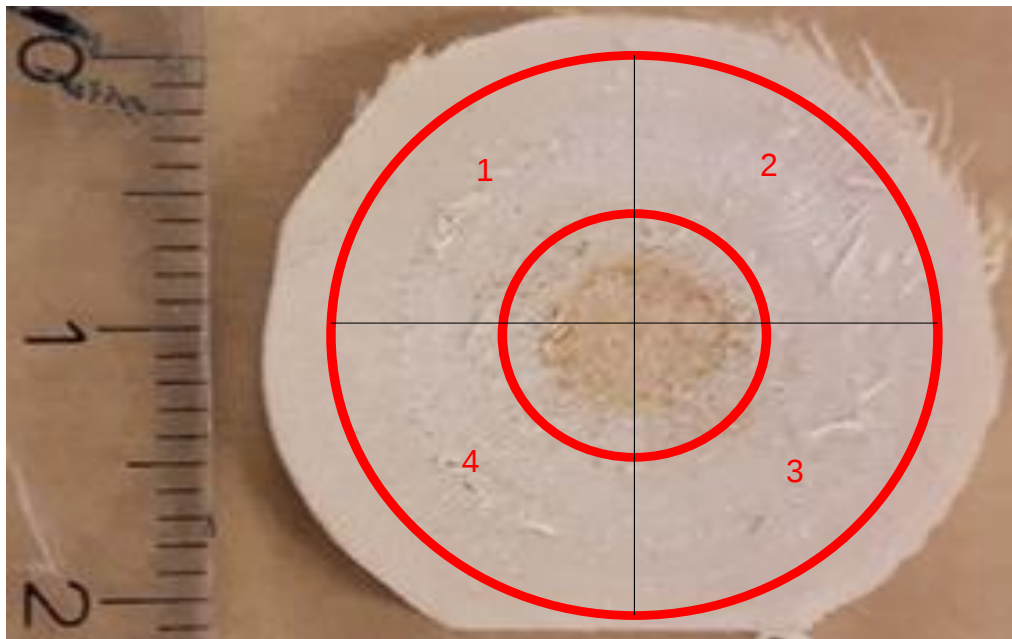


Optimization of biochar properties?

– Porosity vs. process temperature



- ✦ Minor temperature induced changes in macropore structure
- ✦ BET surface area 4 → 8 m² g⁻¹



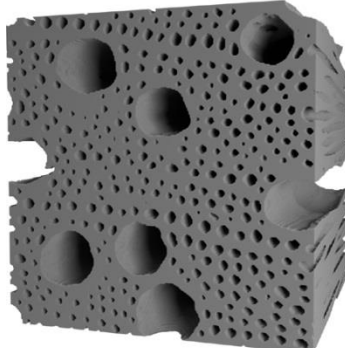
Pyrolysis
temperature
308 - 489 °C

Dried willow

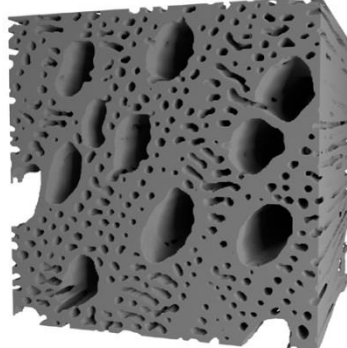
X-Ray Tomography and Helium Ion Microscopy



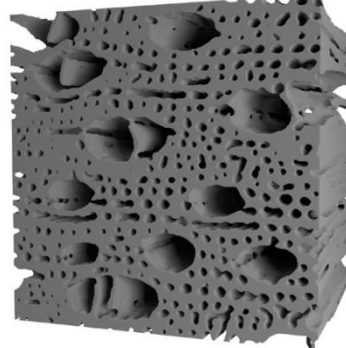
T = 60 °C



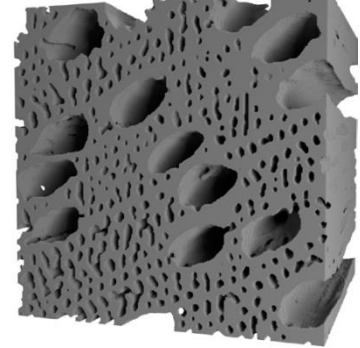
T = 308 °C



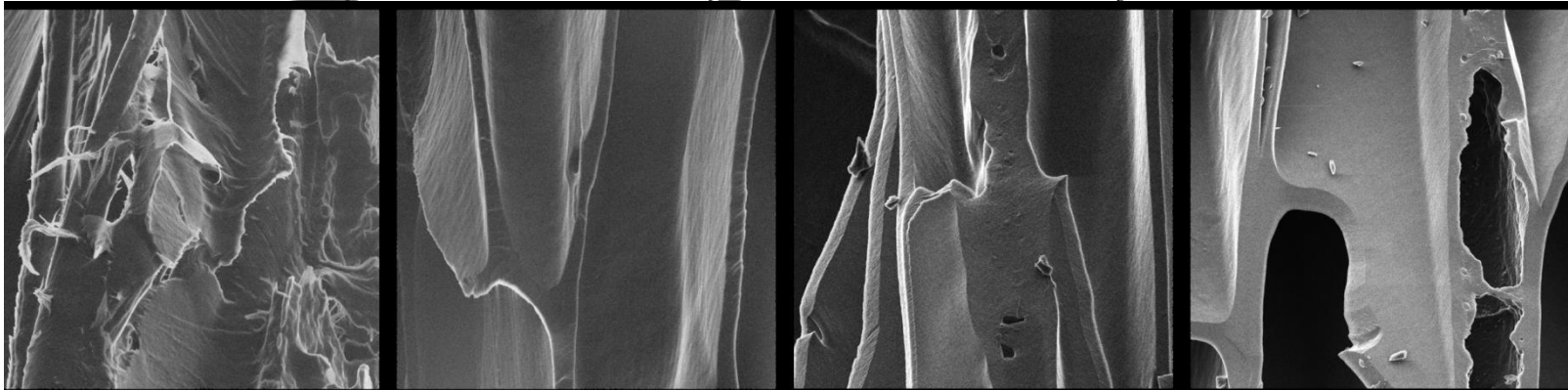
T = 384 °C



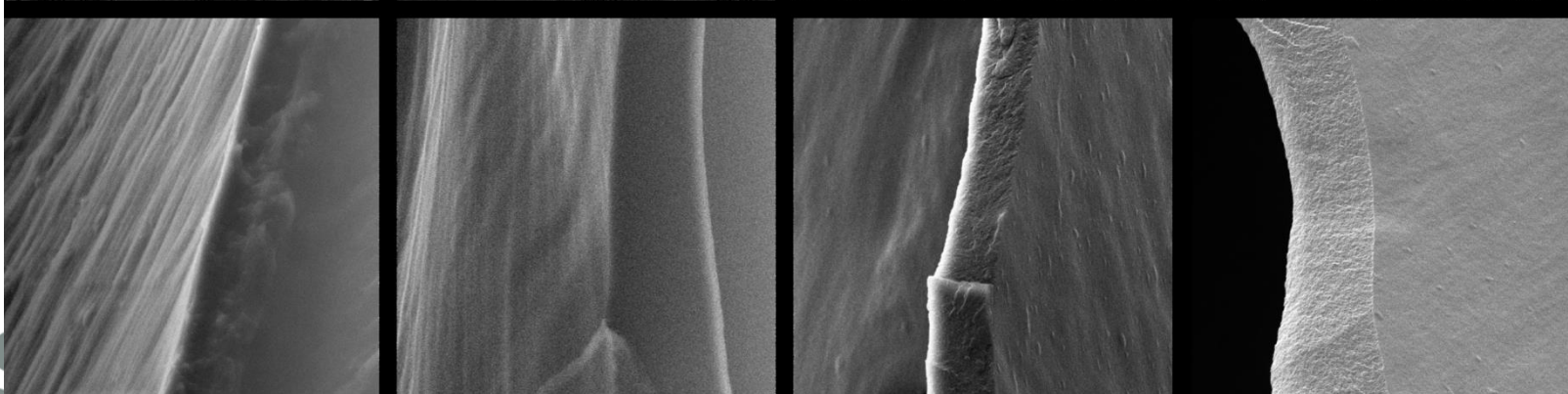
T = 489 °C



20 μm



4 μm



Optimization of biochar properties?

– Surface chemistry vs. process temperature



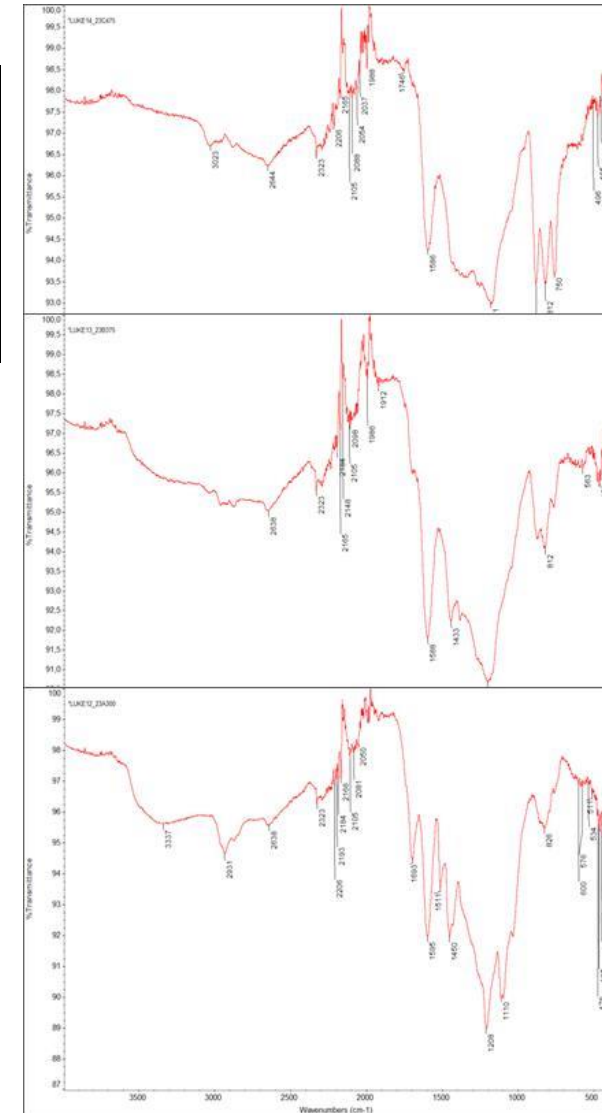
Pyrolysis temperature (°C)	Surface functional groups (mmol kg ⁻¹)			Total acidity (mmol kg ⁻¹)
	Carboxyls	Lactones	Phenols	
300	27	154	na	na
375	19	17	181	217
475	0	0	46	46

✦ Boehm-extraction and FTIR-analysis

✦ → chemistry can be modified

✦ Optimization challenge for biochar producer

✦ Structure vs. chemistry vs. **application**



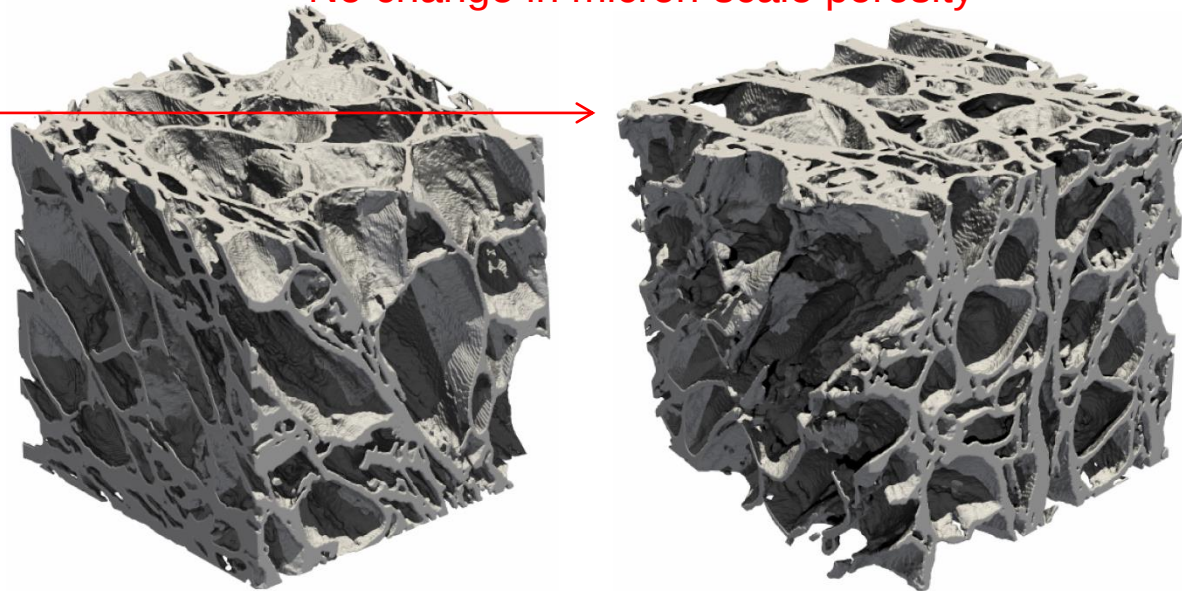
Applications - Activated carbons

- ✦ Micron-scale pores provide pathway to (sub)nano-scale pore regimes
- ✦ Surface area of biochars are generally relatively low
 - ✦ Additional nano-scale porosity via chemical or physical activation
- ✦ BET surface area of Scots Pine Bark ($\text{m}^2 \text{g}^{-1}$)
 - ✦ pyrolysed=19, HTC=4
 - ✦ Phosphoric acid activation
 - ✦ Pyrolysed 339
 - ✦ **HTC 3505**

Non-activated

Activated

No change in micron-scale porosity



Manuscript submitted:

Effects of biomass type, carbonization process and activation method on the properties of bio-based activated carbons
Siipola et al.

Applications – Biochar in soil and growing media

Agriculture

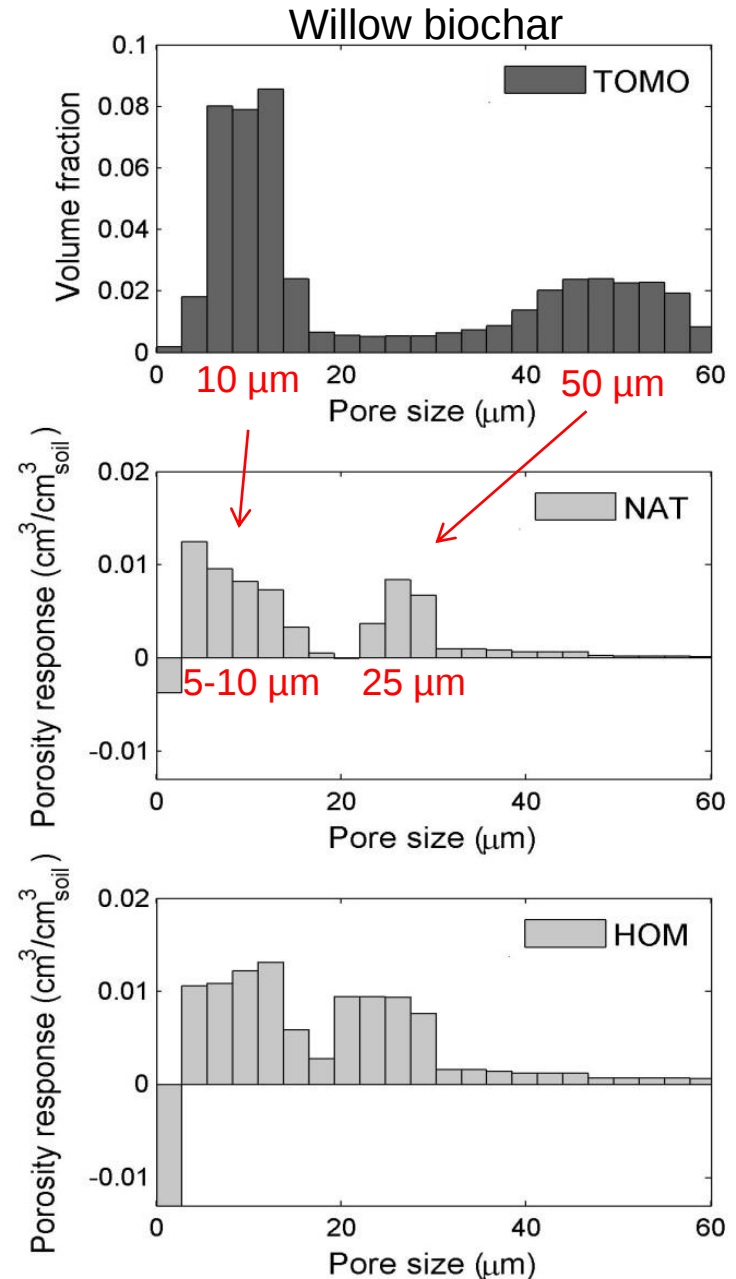


Greenhouse production

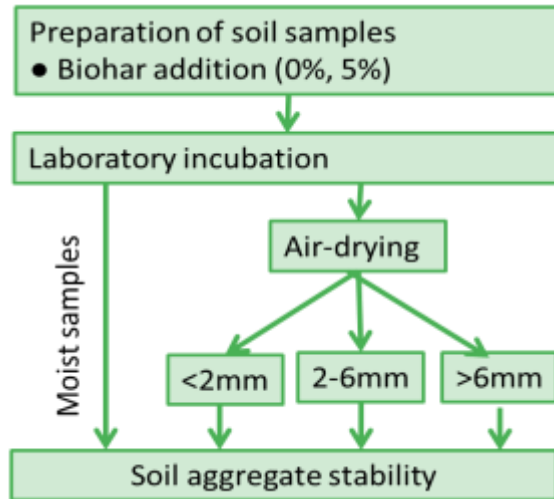


Effect of biochar on soil water retention

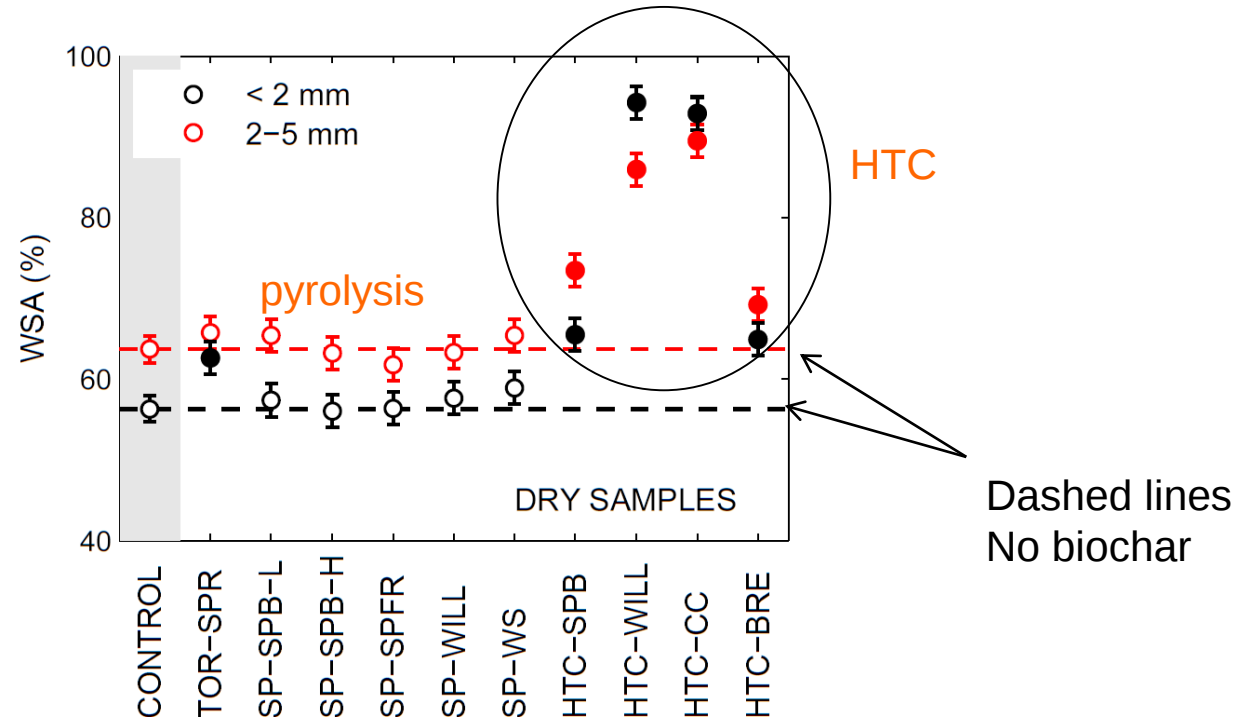
- ✦ Experimental soil: Topsoil from Jokioinen, heavy clay
- ✦ Biochar 5%: Willow biochar pyrolysed at 320 °C
- ✦ Water stored in biochar pores
 - ✦ Significant increase in amount of water that is easily plant available
- ✦ Biochar pore structure + chemistry + soil/growing media texture (particle size distribution)
 - Water retention properties



Biochar and soil structure

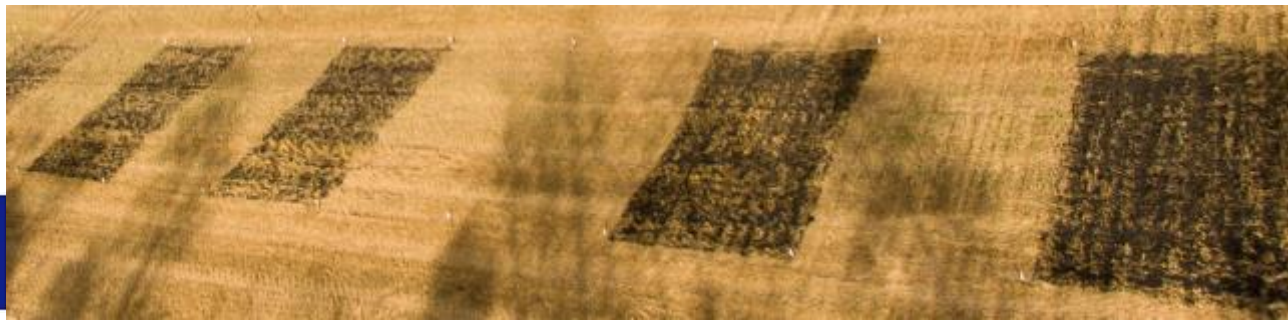


- Wet sieving is a method to study biochar effect on soil structural stability
- How various types of biochars derived from pyrolysis, HTC and torrefaction affects soil aggregate stability?
 - 10 different biochars, chemistry presented earlier



Biochar and soil structure – Field scale

- ✦ Field experiment established 2016
 - ✦ 5 plots with, 5 plots without biochar amendment
 - ✦ Forest residue biochar derived from Raussi's device version 1.0
- ✦ Rain-fall simulation test, soil erosion
 - ✦ Minor effects in the first year
 - ✦ Additional analysis including microbiology at 2nd year
- ✦ Research platform for future projects
 - ✦ Long term effects, financing needed



Applications – Biochar in soil and growing media



- ✦ Boreal climate
 - ✦ “Bulk use” too expensive
 - ✦ High value crops
- ✦ Southern Europe
 - ✦ Dry climate

Unknown drivers:

- unverified biochar properties
- carbon credits
- Etc...

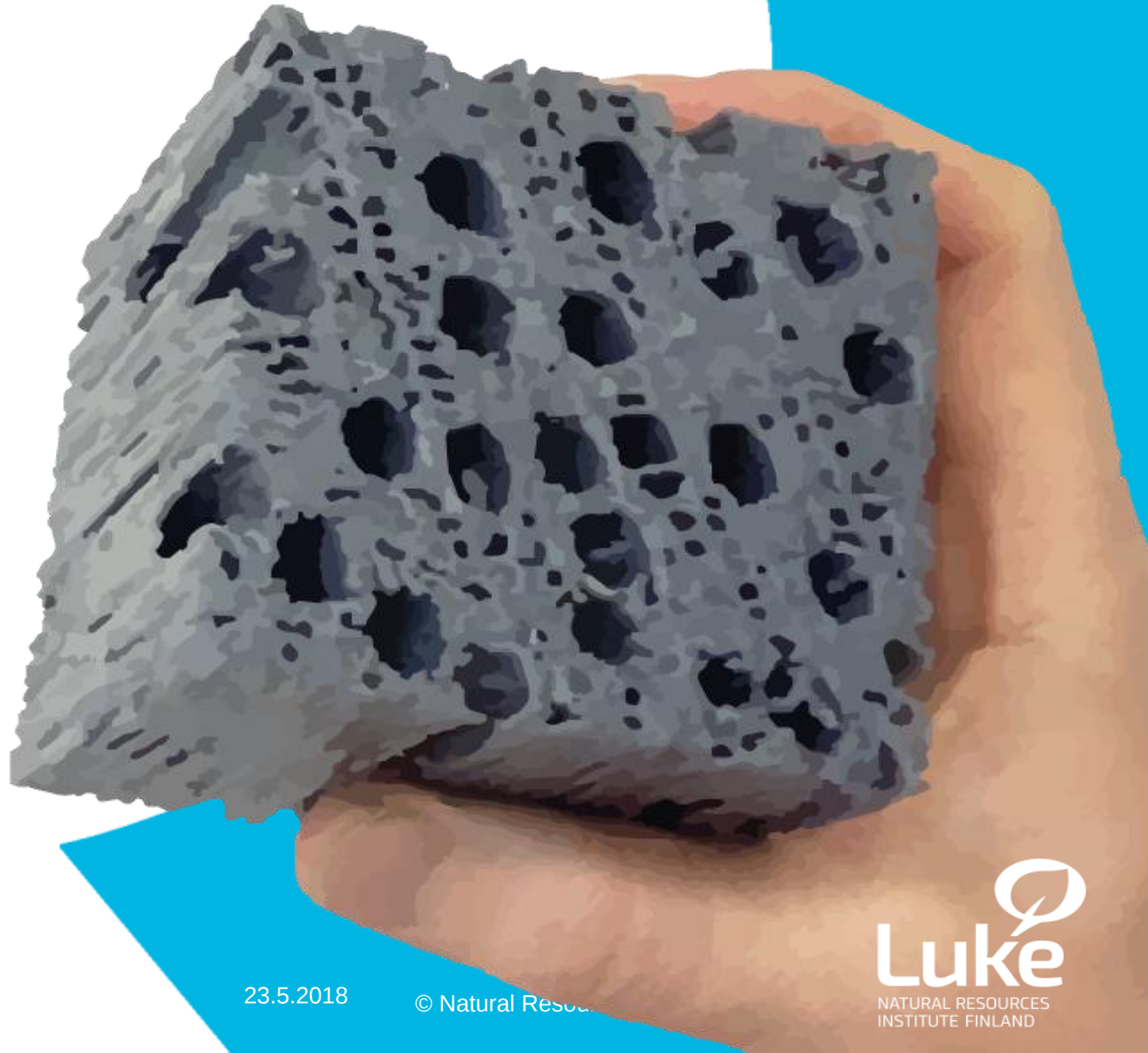


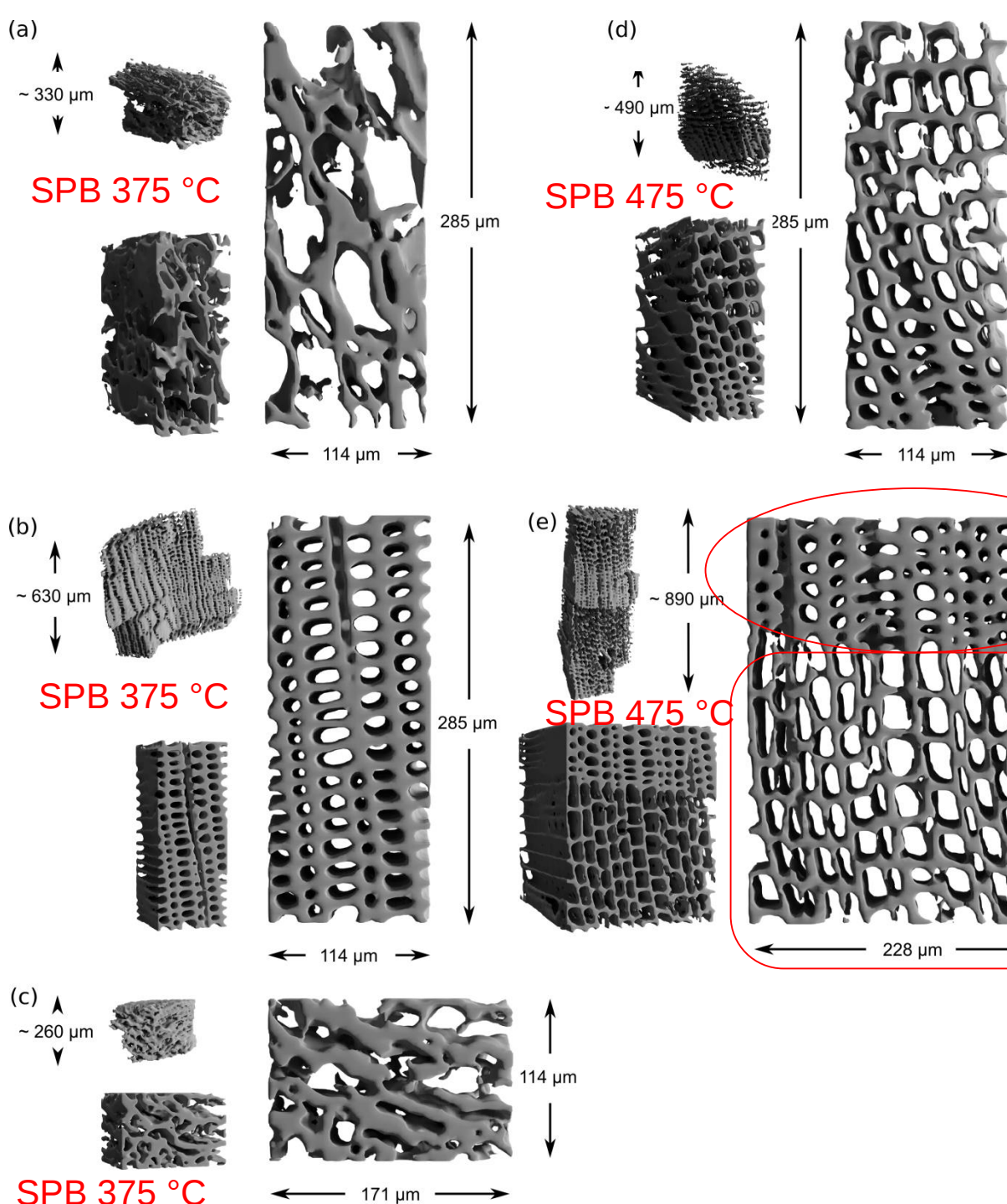
- ✦ Horticulture
 - ✦ Professional greenhouse production
 - ✦ Private gardening
- ✦ Tailored biochars?
- ✦ “Spin off project”
 - ✦ MOSKU together with Biolan Oy

Conclusions

- ✦ Mobile Flip project has generated new and fundamental understanding on biochar properties relevant for many applications
 - ✦ Micron-scale porosity and its effect on Biochar functionality
- ✦ Should we go towards “application oriented thinking”...
 - ✦ What are the properties needed in specific applications?
 - ✦ How can biochar with those properties be produced?
 - ✦ Raw material, process and process parameters (additional activation)
 - ✦ → tailored high value biochars for specific applications
- ✦ ...Or find feasible use for biochar that we can produce in large quantities
 - ✦ E.g. bark from forest industry, other forest and agro residues
- ✦ Business strategy?

Thank you!





Variability in practice



- Scot Pine Bark 375 °C contains both bark and heartwood
 - Robust debarking process
- Scot Pine Bark 475 °C contains summer wood and winter wood
 - Inherent natural variation
- Does heterogeneity challenge concept of “designed biochar”?
- To what extent **biochar producer** can market product with “known properties”